

## REPORT DOCUMENTATION PAGE

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1. REPORT DATE /DD-MM-YYYY/	2. REPORT TYPE	3. DATES COVERED (From - To)		
05 January 2004	Final Performance Report	01 November 99 - 30 April 2003		
4. TITLE AND SUBTITLE		5a. CONTRACT NUMBER		
Basic Studies on Tempered Grain Growth of Relaxor Ferroelectric Crystals and Textured Ceramics		F49620-00-1-0098		
		5b. GRANT NUMBER		
		5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)		5d. PROJECT NUMBER		
Messing, Gary L. Troleir-McKinstry, S.		5e. TASK NUMBER		
		5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)			8. PERFORMING ORGANIZATION REPORT NUMBER	
Pennsylvania State University 110 Technology Center University Park, PA 16802-7000				
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)	
Air Force Office of Scientific Research 4015 Wilson Blvd, Room 713 Arlington, VA 22203-1977			AFOSR	
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT				
Approved for public release, distribution unlimited				
13. SUPPLEMENTARY NOTES				
20040225 161				
14. ABSTRACT				
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15. SUBJECT TERMS				
Piezoelectric, actuators, texture, processing, grain growth				
16. SECURITY CLASSIFICATION OF:		17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE	UU	Gary L. Messing
U	U	U	18	19b. TELEPHONE NUMBER (Include area code) 814-865-2262

Basic Studies on Tempered Grain Growth of Relaxor Ferroelectric  
Crystals and Textured Ceramics

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Abstract

Tempered grain growth (TGG) enables the relatively low cost fabrication of textured ceramics with single crystal-like properties, as well as single crystals. In TGG, nucleation and growth of the desired crystal on aligned single crystal template particles results in an increased fraction of oriented material with heating. To serve as the preferred sites for epitaxy and subsequent oriented growth into the matrix, the template particles need to be single crystal and chemically stable up to the growth temperature.

The resulting ceramics show texture levels up to 90%, and significant enhancements in the piezoelectric properties relative to randomly oriented ceramics with comparable densities. The  $d_{33}$  coefficients of highly textured PMN-32.5PT ceramics were found to be ~1.2-1.5 times greater than randomly-oriented samples. The unipolar strain-field measurements (<5 kV/cm) of ~90%-textured PMN-32.5PT ceramics produced  $d_{33}$  coefficients as high as 1150 pC/N with relatively low piezoelectric hysteresis. Electrical and electromechanical property characterization of  $<001>_{pc}$  textured  $(Na_{1/2}Bi_{1/2})TiO_3$ -5.5 mol% BaTiO<sub>3</sub> rhombohedral ceramics showed 0.26% strain at 70 kV/cm, and large field  $d_{33}$  coefficients over 500 pC/N were obtained for highly textured samples (f~90%). Reasons for why the high field dielectric and

electromechanical properties are more hysteretic than those of single crystals are discussed.

## Introduction

Currently, inorganic piezoelectric crystals and ceramics are applied to a broad range of applications important to the Air Force and other branches of the DOD. These applications can be categorized into four major groups: 1) generators that convert mechanical into electrical energy, 2) sensors that convert mechanical force into a electrical signal, 3) sonic and ultrasonic transducers that convert electrical into mechanical energy), and 4) actuators that convert electrical signals into a mechanical displacement.<sup>(1,2)</sup> Therefore, piezoelectric materials find applications as high quality igniters, hydrophones, microphones, micro-motors and -pumps, buzzers, loud speakers, micropositioners, delay lines, video head positioners, sonar, medical ultrasound equipment, and multiple other electromechanical devices.

Materials displaying piezoelectric, electrostrictive, piezomagnetic, magnetostrictive, photostrictive, thermoelastic, or shape memory physical characteristics may be applied to actuator applications. Currently, inorganic piezoelectric materials are the most widely used, especially in the case of high performance actuators, due to their high generative force, relatively accurate displacement, and high frequency operation capabilities.

The most widely used piezoelectric single crystal materials are  $\alpha$ -quartz ( $\text{SiO}_2$ ), lithium niobate ( $\text{LiNbO}_3$ ), and lithium tantalate ( $\text{LiTaO}_3$ ). These materials are extensively used in industrial applications as a result of their temperature stability, wide operating temperature range, and ease of crystal growth as large, defect-free single

crystals. The most widely used polycrystalline ceramics for piezoelectric applications are  $\text{BaTiO}_3$  and  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  (PZT), which both have the perovskite structure ( $\text{ABO}_3$ ). PZT shows the maximum piezoelectric response at compositions near the morphotropic phase boundary (MPB) between the tetragonal and rhombohedral phases ( $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ ). Since there are two equally stable phases at this composition, there remain multiple allowable domain orientations which are associated with these phases, allowing for efficient poling. The properties and stability of both  $\text{BaTiO}_3$  and PZT are commonly altered through the substitution of various isovalent or aliovalent ions for either the A or B sites of the perovskite structure.

For a high performance actuator, the piezoelectric material must show high thermal stability, high strain with an applied electric field, low mechanical loss, and thus, low hysteresis.<sup>(2)</sup> Therefore, piezoelectric materials for actuator applications should possess a high phase transition, or Curie, temperature, a high piezoelectric coefficient ( $d_{ij}$ ), and in some cases a high mechanical quality factor. In addition to the above mentioned requirements, for high performance medical transducer applications, a high electromechanical coupling coefficient ( $k_{ij}$ ) is required since the  $k_{ij}$  dictates the bandwidth of the transducer.

The next generation of actuators and transducers requires a significant increase in some or all of the typical figure of merit coefficients ( $d_{ij}$ ,  $k_{ij}$ , and  $Q_M$ ) which describe the performance of the piezoelectric materials. The various solid solutions based on PZT ceramics are the most promising for many piezoelectric applications, but the degree of improvement in the PZT compositions has been modest from the 1970's to the late 1990's. The inability to grow single crystals of PZT near the MPB of a usable size and

quality has slowed progress towards the next generation of novel high strain piezoelectric materials.

Although large single crystals of PZT at the MPB composition have not been been grown, other Pb-based relaxor ferroelectric-PbTiO<sub>3</sub> compositions at their MPB can be grown by conventional high temperature solution growth. This was first shown in the early 1980's.<sup>(4,5)</sup> and more recently by Park and Shroud<sup>(3)</sup>. The Pb-based relaxor ferroelectric-PbTiO<sub>3</sub> compositions also have the basic perovskite structure, like PZT, but the B-sites are occupied by various off-valent ions. Kuwata *et al.*, for single crystal Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub> (PZN-PT), and Park and Shroud (1997)<sup>(3)</sup>, for both single crystal PZN-PT and Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub> (PMN-PT), reported piezoelectric coefficients ( $d_{33}$ ) between 1500-2500 pC/N and electromechanical coupling coefficients ( $k_{33}$ ) >0.9 with low hysteresis. It should be noted that the best PZT (PZT-5H)<sup>(6,7)</sup> shows  $d_{33}$  of ~600 pC/N and  $k_{33}$  of ~0.70-0.75. PZT-5H is considered a “soft” ferroelectric, since its domain state can be easily altered by a small electric field or mechanical stress. However, under large field drives soft PZT shows undesirably large hysteresis, dielectric and mechanical loss, and heat generation.<sup>(3)</sup> Acceptor doping the PZT to form a “hard” PZT (PZT-4, PZT-8, PZT-7A) eliminates the large hysteresis under high drive levels, but it also lowers the piezoelectric coefficients ( $d_{33}$ <300 pC/N) and the electromechanical coupling coefficients to some degree ( $k_{33}$ <0.7). Therefore, the ultrahigh piezoelectric coefficients, electromechanical coupling coefficients, strain levels, and low hysteresis values observed for the PZN-PT and PMN-PT single crystals represent a significant step forward in piezoelectric actuation materials.

The enhanced piezoelectric response and low hysteresis of rhombohedral PZN-PT and PMN-PT single crystals were observed primarily for <001> crystal cuts. Crystal cuts offset from this orientation displayed lower piezoelectric response and increased hysteresis. The elevated piezoelectric response for the [001] oriented rhombohedral single crystals was credited to the rotation of the polarization vector from the <111> to [001].<sup>(3)</sup> The low hysteresis in the rhombohedral crystals has been attributed to a stable domain configuration in the <001>. The manipulation of the crystal orientation in order to access a specific stable domain configuration had been termed “domain engineering.”

It has been demonstrated that by orienting (texturing) the grain structure of the ceramic, the macroscopic symmetry can reflect that of its single crystal counterpart. The decrease in symmetry from the random polycrystalline ceramic to the single crystal state depends on the texture dimensionality (fiber or sheet texture) and the distribution of the grain crystallographic orientation. Multiple piezoelectric compositions have been textured, and the texturing always leads to an increase in the property anisotropy. When the composition was textured in the polarization direction, there was always an increase in the piezoelectric coefficient relative to random ceramics due to the increase in poling efficiency. All but one of the piezoelectric compositions textured possess relatively low symmetry, and thus, these compositions show an innate ability to form anisometric grains as well as anisotropic grain growth behavior. This behavior assists in the initial orientation of the grain structure during green processing and the further texture development due to anisotropic grain growth during high temperature treatment. The  $\text{BaTiO}_3$  and  $\text{Bi}_{0.5}(\text{Na}_{0.35}\text{K}_{0.15})_{0.5}\text{TiO}_3$  compositions are the only piezoelectric compositions textured from cubic prototype groups reported in literature.<sup>(8,9)</sup>

The primary objectives of the research program were to produce single crystal and fiber-textured piezoelectric ceramics by template grain growth (Figure 1). Of particular interest were compositions near the MPB, in the <001> directions so that the single crystal electromechanical properties observed for <001>-cuts of single crystals can be accessed. Single crystals of BaTiO<sub>3</sub> and Zr-doped BaTiO<sub>3</sub> were prepared by TGG and compared to single properties. Techniques for texturing PMN-PT and (Na<sub>1/2</sub>Bi<sub>1/2</sub>)TiO<sub>3</sub>-BaTiO<sub>3</sub> (NBT-BT) NBT ceramics by TGG were developed and the properties compared to those of single crystals. This work is extensively reported in the archival, peer-reviewed literature<sup>(10-30)</sup> and three Ph.D. dissertations<sup>(31-33)</sup> which are readily available from the University of Michigan Press.

### **Single Crystals<sup>(10-13)</sup>**

Templated grain growth is an inexpensive method for producing single crystals of various materials relative to current high temperature solution techniques. It is an alternative to conventional high temperature solution techniques with similar growth rates. Single crystals of BaTiO<sub>3</sub> were grown by templated grain growth. Millimeter size single crystals of BaTiO<sub>3</sub> were produced by heating a 97% dense polycrystalline matrix with a Ba/Ti ratio < 1.00 in contact with specifically oriented BaTiO<sub>3</sub> single crystals at temperatures above the eutectic temperature. The interface moved into the polycrystalline matrix at growth rates ranging from ~590-790  $\mu\text{m}/\text{h}$ , ~180-350  $\mu\text{m}/\text{h}$ , and ~42-59  $\text{m}/\text{h}$  for {111}, {100}, and {110} oriented single crystal templates, respectively (Figure 1).<sup>(12)</sup> The growth rates slowed when lower surface energy facets were formed for {111} and {100} oriented templates and as a result of matrix coarsening.

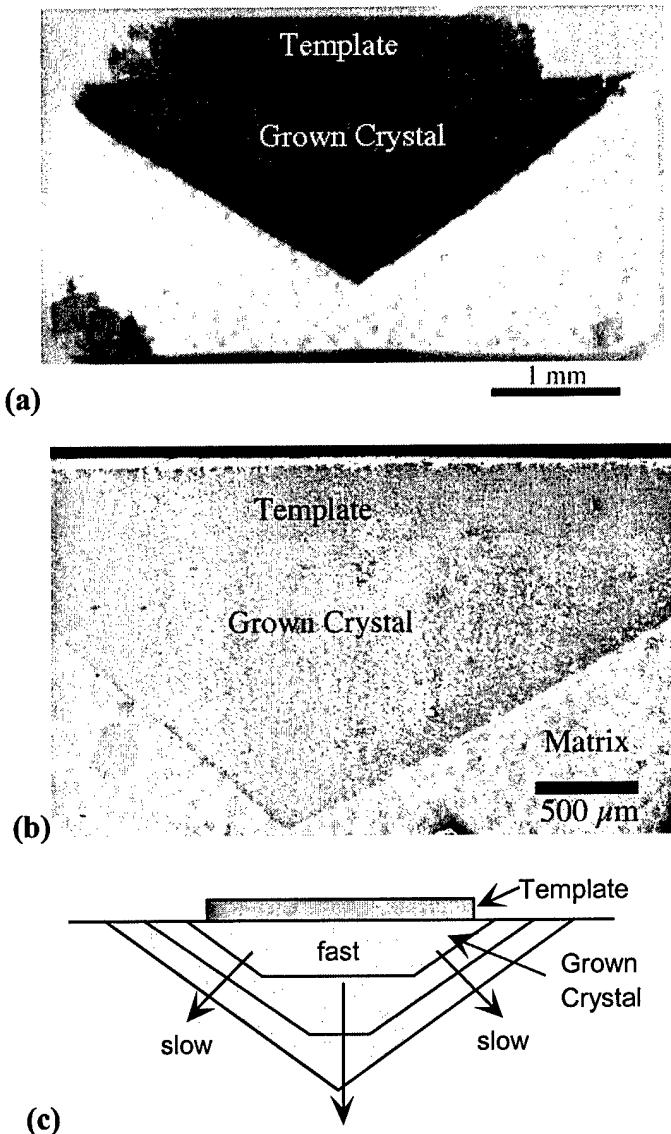


Figure 1 (a) Optical micrograph of a  $\text{BaTiO}_3$  crystal grown into a Ti-rich polycrystalline matrix after 8 h at 1350°C from a {100} oriented template (Bar = 1 mm). (b) SEM micrograph of a  $\text{BaTiO}_3$  crystal grown into a Ti-rich polycrystalline matrix after 5 h at 1350°C from a {111} oriented template (Bar = 500  $\mu\text{m}$ ). (c) Schematic showing habit plane formation for growth from {100} oriented templates.<sup>(12)</sup>

Single crystals of  $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  were grown by TGG on  $\text{BaTiO}_3$  single crystals.

Millimeter size crystals of  $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  of  $x = 4.5, 5.0$  and  $8.0$  mol% Zr were produced

by heating to 1350°C for 30 h. To facilitate boundary migration, the ceramic compact was made 3 mol% TiO<sub>2</sub> excess to induce liquid formation and thus accelerate growth rates at 1350°C. The 4.5 and 5.0 mol% Zr-doped crystals were orthorhombic at room temperature. For a psuedocubic orientation <001>, these crystals showed a remanent polarization of 13  $\mu$ C/cm<sup>2</sup> and a high field  $d_{33}$  of 340-355 pC/N. The 4.5 mol% Zr-doped crystal had a coupling coefficient of 0.74. These results clearly demonstrate the potential for growing high quality crystals with controlled orientation and a range of compositional doping.

#### **Textured Piezoelectrics – PMN-PT<sup>(14-23)</sup>**

A poled <001>-textured ceramic is a close match to the macroscopic symmetry displayed by a fully <001>-poled PMN-PT single crystal. This allows the textured PMN-PT ceramic to benefit from the concept of domain engineering in order to access the low hysteresis and extraordinary high piezoelectric response of the single crystals. In addition to the enhancement in the piezoelectric properties, processing problems encountered during the growth of the single crystal PMN-PT can be circumvented by texturing PMN-PT by conventional ceramic processing techniques. Single crystal growth of PMN-PT is limited by low production efficiency, high production cost, long growth time, small product size, limited shape forming capability, and compositional heterogeneity. Standard ceramic processing techniques which provide the proper shear force to align the ceramic platelet or fiber particles during the green and final processing stages enable the production of low cost, high yield, textured PMN-PT ceramics of various sizes and shapes.

TGG entails the mechanical alignment of a relatively small volume fraction of template particles within a ceramic matrix during green processing. With thermal treatment of the green ceramic, the template particles grow at the expense of the finer matrix powder in order to increase the volume fraction of textured material within the ceramic.<sup>(16)</sup>

Rhombohedral  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{PbTiO}_3$  (PMN-PT) single crystals near the morphotropic phase boundary (MPB) show enhanced strain levels combined with exceedingly large piezoelectric and electromechanical coupling coefficients for <001>-oriented and -poled crystal cuts. In principle, <001> fiber-textured PMN-PT ceramics should possess a high fraction of the electromechanical and dielectric properties displayed by their single crystal counterparts.

The TGG process requires the template to have a strong epitaxial relationship to the crystal structure of the matrix composition. The template must also show the proper size and aspect ratio, so it may be mechanically aligned and grow at the expense of the fine matrix. Potential template particles with a layered-perovskite and tungsten-bronze structure ( $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ,  $\text{Sr}_3\text{Ti}_2\text{O}_7$ ,  $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ , and  $\text{Sr}_2\text{Nb}_2\text{O}_7$ ) were shown to form a cubic-pyrochlore phase when reacted with the PMN-PT matrix at temperatures  $>850^\circ\text{C}$ . Some perovskite templates (including forms of  $\text{PbTiO}_3$ ,  $\text{SrTiO}_3$ , and  $\text{BaTiO}_3$ ) were shown to dissolve into the PMN-PT matrix or intergranular  $\text{PbO}$ -phase, minimizing their utility in templating the desired PMN-PT composition.  $\text{BaTiO}_3$  platelet crystals were found to be suitable templates for the TGG of PMN-PT. The  $\text{BaTiO}_3$  crystals were stable within the PMN-PT matrix at temperatures  $>850^\circ\text{C}$  and they were shown to act as proper heteroepitaxial substrates for templated growth of the PMN-PT composition (Figure 2).

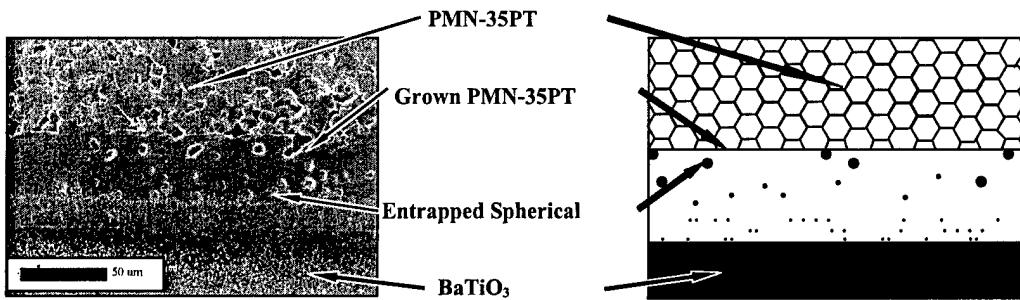


Figure 2. Tempered grain growth of a PMN-35PT single crystal on a (100)-BaTiO<sub>3</sub> in a PMN-PT matrix containing excess PbO sintered at 1150°C for 15 min.<sup>(17)</sup>

The TGG kinetics from {001}-, {110}-, and {111}-BaTiO<sub>3</sub> crystals were observed and fit to a diffusion-controlled model with a non-constant driving force. The crystal growth kinetics were shown to be limited by the decrease in the driving force due to the coarsening and shape change of the matrix grains. The growth kinetics were also shown to be dependent upon the intergranular liquid content and the template orientation. Excess PbO concentration >1 wt% was shown to accelerate the growth of the crystal layer. The <111> crystallographic orientation was found to be the fastest growing direction with the <001>-direction as the slowest.

PMN-32.5PT ceramics were fiber-textured by initially aligning {001}-BaTiO<sub>3</sub> platelets (~75-150 μm in diameter) within the matrix by tapecasting. Dense PMN-32.5PT ceramics (1 wt% excess PbO) with a 5 vol% template concentration were <001>-textured to a texture fraction ~0.90 with an annealing time >1 h at 1150°C. The degree of texturing was slightly increased with an increase in annealing time and template concentration (10 vol% templates). The decrease in texturing rate was attributed to the

decreasing driving force for growth due to the coarsening and shape change of the matrix. The texturing kinetics was also found to decrease after longer annealing times ( $>1$  h) due to grain impingement and porosity development around the templated grains.

An increase in texture fraction of the  $\{001\}$ -BaTiO<sub>3</sub> templated PMN-32.5PT ceramics produced an increase in the piezoelectric, electromechanical coupling, and compliance coefficients over randomly-oriented samples of the same composition. The  $d_{33}$  coefficients of highly textured PMN-32.5PT ceramics (~90%-textured) were found to be  $\sim 1.2$ - $1.5$  times greater than randomly-oriented samples and the maximum strain was 0.28% (Figures 3 and 4). The unipolar strain-field measurements ( $<5$  kV/cm) of ~90%-textured PMN-32.5PT ceramics produced  $d_{33}$  coefficients as high as 1150 pC/N with relatively low piezoelectric hysteresis. Additional PbO was purposely added to the PMN-32.5PT matrix in order to increase the TGG kinetics and drive the samples to full-texture. Regardless of the texture quality, the presence of the intergranular PbO-phase resulted in a low dielectric constant ( $\epsilon_{rt}^{poled} < 3000$ ) for the textured samples, which remained similar to random PMN-32.5PT samples containing excess PbO. The presence of the residual BaTiO<sub>3</sub> templates within the templated grains did not alter the transition temperatures of the PMN-32.5PT ceramics. This suggests that BaTiO<sub>3</sub> did not dissolve into the matrix, further emphasizing the relative stability of the BaTiO<sub>3</sub> template particles. The magnitudes of the dielectric and piezoelectric properties were also found to be limited by the presence of misoriented templated-grains, unoriented grains, porosity, and the remnant BaTiO<sub>3</sub> templates.

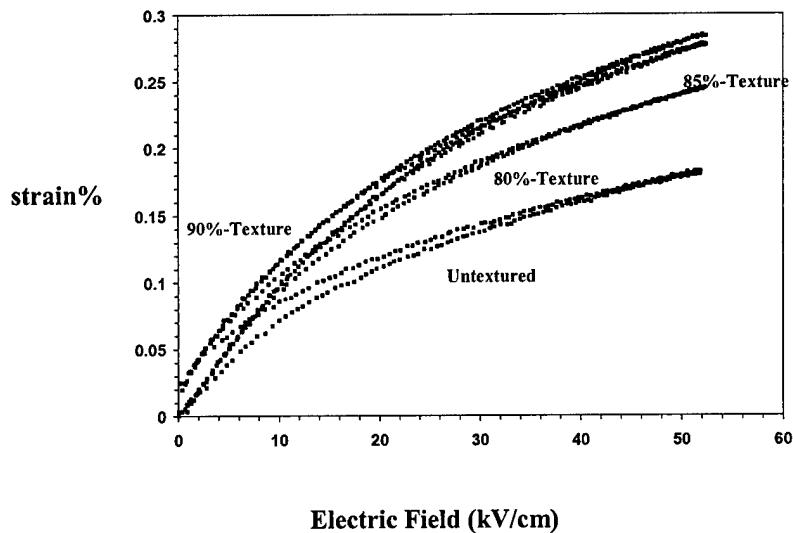


Figure 3. Unipolar strain-electric field curves of PMN-32.5PT ceramics containing 5 vol% BaTiO<sub>3</sub> templates (PMN-32.5PT-5BT) displaying various degrees of texture.<sup>(20)</sup>

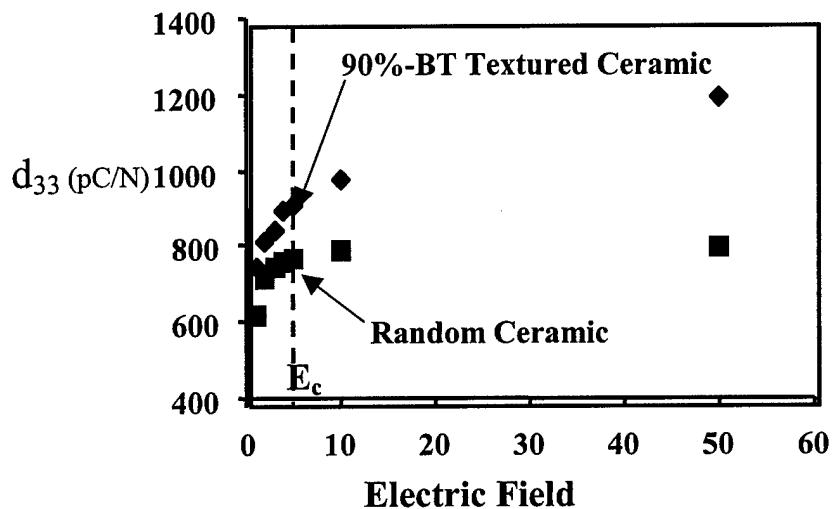


Figure 4. Low-field (<5 kV/cm)  $d_{33}$  coefficients measured from unipolar strain-electric field curves of a ~90%-textured PMN-32.5PT-5BT ceramic and a random PMN-32.5PT ceramic measured to maximum unipolar fields between 1-50 kV/cm.

## Textured Piezoelectrics – NBT-BT<sup>(24-27)</sup>

Sodium bismuth titanate modified with barium titanate,  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-BaTiO}_3$  (NBT-BT), is a candidate lead-free piezoelectric material which has been shown to have comparatively high piezoelectric response. In this work, textured  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-BaTiO}_3$  (5.5mol% BaTiO<sub>3</sub>) ceramics with  $<100>_{pc}$  (where pc denotes the pseudocubic perovskite cell) orientation were fabricated by Tempered Grain Growth (TGG) or Reactive Tempered Grain Growth (RTGG) using anisotropically shaped template particles. In the case of TGG, molten salt synthesized SrTiO<sub>3</sub> platelets were tape cast with a  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-5.5mol%BaTiO}_3$  powder and sintered at 1200°C for up to 12 hours. For the RTGG approach, Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> (BiT) platelets were tape cast with a Na<sub>2</sub>CO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and BaCO<sub>3</sub> powder mixture and reactively sintered. The TGG approach using SrTiO<sub>3</sub> templates gave stronger texture along [001] compared to the RTGG approach using BiT templates. The grain orientation distribution in the [001], as measured by x-ray rocking curve (and also OIM), has a full width at half maximum of ~8° and a texture fraction of 80% for the samples sintered at 1200°C for 12 hours in O<sub>2</sub>.

Electrical and electromechanical property characterization of randomly oriented and  $<001>_{pc}$  textured  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-5.5 mol% BaTiO}_3$  rhombohedral ceramics showed 0.26% strain at 70 kV/cm, and large field d<sub>33</sub> coefficients over 500 pC/N have been obtained for highly textured samples (f~90%). The d<sub>33</sub> coefficient from Berlincourt measurements was d<sub>33</sub>~200 pC/N. The materials show considerable hysteresis. The presence of hysteresis in the unipolar-electric field curve may be linked to the ferroelastic phase transition seen in the  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$  system on cooling from high temperature at ~520°C.

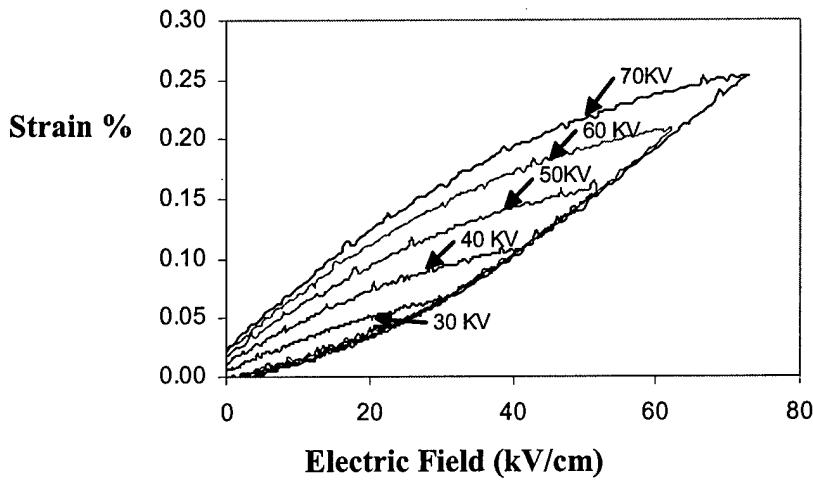


Figure 5. Unipolar maximum strain of textured  $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5% BaTiO<sub>3</sub> ceramics textured with 5 vol% SrTiO<sub>3</sub>.

The macroscopic physical properties (remanent polarization, dielectric constant, and piezoelectric coefficient) of random and textured  $([\text{001}]_{\text{pc}})$  rhombohedral perovskites were estimated by linear averaging of single crystal data. However, the complete polarization, dielectric, and piezoelectric tensors are not available for NBT-BT single crystals. Therefore, the properties of lead based (PZT, 52/48) rhombohedral ferroelectric single domain-single crystals, whose properties (polarization, dielectric and piezoelectric) were computed using Landau-Ginsburg-Devonshire phenomenological theory (by Haun et al.), were used in the calculations for random and textured cases. Based on the averaging calculations for a ceramic with rhombohedral symmetry, the remanent polarization was expected to decrease but the other properties like dielectric constant and piezoelectric coefficient were expected to increase as the texture fraction in the ceramic increases. The experimental findings were in agreement with the trends in the calculations.

## **Summary**

TGG is a significantly lower cost manufacturing process than single crystal growth processes. We have made major strides in producing high quality, textured piezoelectric materials that possess a large portion of the single crystal properties<sup>(27-30)</sup>. The growth of oriented PMN-PT by TGG is reasonably well understood as is the material system for obtaining high quality PMN-PT.

As a result of the high texture fraction, the resulting materials show considerably better piezoelectric properties than randomly oriented bulk ceramics. For example, textured PMN-PT has a  $d_{33}$  of 1300 pC/N at 10 kV/cm. This is at least two times better than random PMN-PT. There is significantly more hysteresis in the strain-field curve behavior of textured ceramics than observed with single crystals or random ceramics. The hysteresis is clearly a result of the quality of the grain orientation although other factors (e.g., clamping of single crystal grains in a fine grain matrix, presence of an inert template in the matrix) play a role. Thus, there is a need for further research to determine means for producing textured ceramics with higher texture fraction and narrower orientation distribution function.

## **Research participants**

Gary L. Messing, Susan Trolier-McKinstry, James H. Adair, Paul Rehrig, Edward Sabolsky, Huseyin Yilmaz, Ender Suvaci, and Kyung-Sik Oh

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